ADELAIDE
UNIVERSITY
AUSTRALIA

Department of Chemistry

ORGANOTIN COMPOUNDS FOR CATALYSIS

A Thesis Submitted for the

Degree of Master of Science

by

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ADDENDUM

- The abbreviation for Electrospray Mass Spectrometry is ESMS.
- 2.16: Table 2.8: The absolute structure parameter is -0.3(2).
- 2-17: The symmetry operation is *x, 2-y, 1/2+z*.
- 3-13: The last sentence should read 'Hence, a detailed analysis and discussion of the results is not included in this thesis, as the author did not undertake the experiments.'
- 3-15: Fig. 3.2: The C(3)-C(5) atoms of a butyl group were found to be disordered so that two positions (50% occupancy) were found for each of C(3) and C(5).
- 3-28: Fig. 3.5: The tin-bound n-butyl group was found to be disordered so that two positions (50% occupancy) were found for the C(22)-C(24) atoms.
- 5-4: 5.2.2: The mass of trimesic acid used was 0.111 g and three molar equivalents of organotin were used.
- 5-7: 5.2.5: The volume of organotin used was 100 μL and varying molar equivalents (one, three and six) of dithiocarbamate were used.
- 6-1: Paragraph 1: The last line should read $[R_2(Cl)SnO_2C]_3C_6H_3$.

DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and, to the best of my knowledge, contains no material previously published or written by another person, except where due reference is made.

I consent to the thesis being made available for photocopying and loan if accepted for the award of the degree.

David Clarke
June 2001

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ABSTRACT

There were three major aims for this project. The first major aim was to explore alternative synthetic pathways to high nuclearity organotin clusters that may have use as catalysts. Complexes of the type $(R_3SnO_2C)_3C_6H_3$ were prepared and characterised by infrared and NMR spectroscopy, and in two cases X-ray crystallography. These trinuclear compounds feature tetrahedral tin centres, owing to the monodentate coordination of the carboxylate groups. Attempts to substitute one phenyl group by X (X = Cl, OAc, OH) to form $[Ph_2(X)SnO_2C]_3C_6H_3$ type complexes, attempted in order to extend the trinuclear framework, were unsuccessful.

The second major aim of this project was to produce precursors for organotin-oxo clusters. This involved preparation of complexes of the type $RSnL_3$, $RSnL_2Cl$ and $RSnLCl_2$, where L is a dithiocarbamate anion ($^-S_2CNR_2$). ESMS was used to examine whether the precursor complexes led to specific cluster formation upon the addition of base. The results of the ESMS suggested the formation of a variety of clusters rather than a specific cluster. These complexes were characterised by spectroscopy and in four cases, X-ray crystallography, confirming the formation of seven ($RSnL_3$), six ($RSnL_2Cl$) and five ($RSnLCl_2$) coordinate species.

The third major aim of this project was to form mixed dinuclear tin species using 2- and 4-mercaptobenzoic acids as ligands. These complexes were characterised by spectroscopic methods and in one case by X-ray crystallography, which confirmed that the molecules do not aggregate in the solid state.

ABBREVIATIONS

The following abbreviations are used in this thesis.

Me	methyl	t	triplet
Et	ethyl	q	quartet
^{i}Pr	*iso*-propyl	sext	sextet
^{i}Bu	*iso*-butyl	m	multiplet
^{t}Bu	*tert*-butyl	br	broad
Ph	phenyl	obs	obscured
Cy	cyclohexyl	n.o.	not observed
Bu	butyl	IR	infrared
Me	methyl	w	weak
2mba	2-mercaptobenzoic acid	m	medium
4mba	4-mercaptobenzoic acid	s	strong (IR)
CH_2Cl_2	dichloromethane	vs	very strong
DMSO	dimethylsulphoxide	br	broad
Å	Angstroms	Hz	Hertz
°C	degrees Celsius	MHz	Mega Hertz
K	Kelvin	ppm	parts per million
NMR	Nuclear Magnetic Resonance	TMS	tetramethylsilane
s	singlet (NMR)	Me_4Sn	tetramethyltin
d	doublet	δ	chemical shift in ppm
dd	doublet of doublets	λ	wavelength
dt	doublet of triplets	R	alkyl, aryl

ν(X-Y)	Stretching frequency of the X-Y bond in cm^{-1}
$^{x}J_{A-B}$	coupling constant between nuclei A and B over *x* bonds in Hz

^{1}H NMR	proton-1 NMR
^{13}C NMR	proton decoupled carbon-13 NMR
^{119}Sn NMR	tin-119 NMR
HMQC	Heteronuclear Multiple Quantum Coherence
HMBC	Heteronuclear Multiple Bond Connectivity
FW	formula weight
V	Volume
Z	no. of molecules in the asymmetric unit
D(calc)	calculated density in g cm^{-3}

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